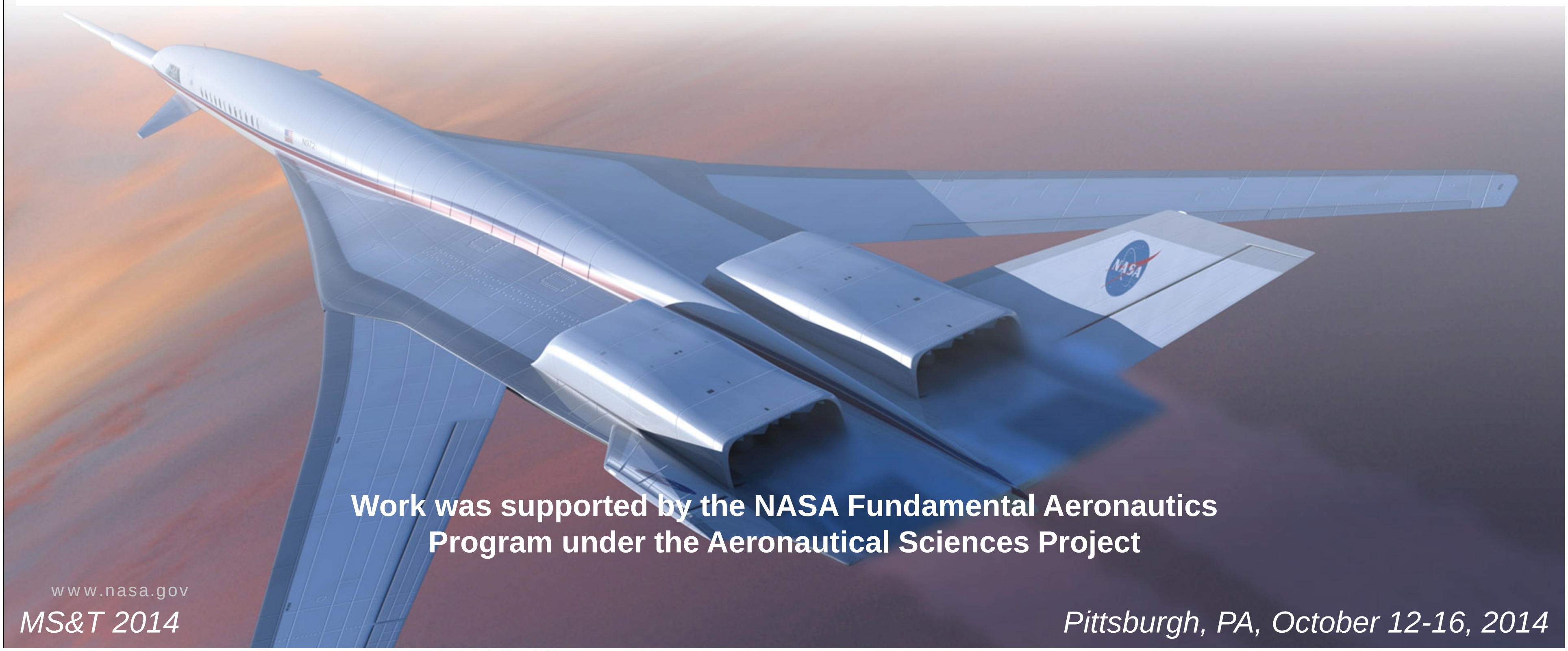
High Temperature Multilayer Environmental Barrier Coatings Deposited Via Plasma Spray–Physical Vapor Deposition

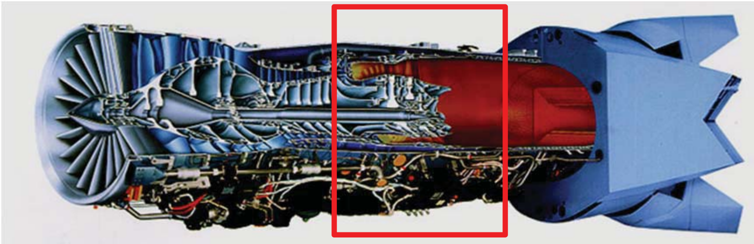
B. J. Harder and D. Zhu
NASA Glenn Research Center, Cleveland OH 44135
M. P. Schmitt and D. E. Wolfe
The Pennsylvania State University, University Park PA 16802

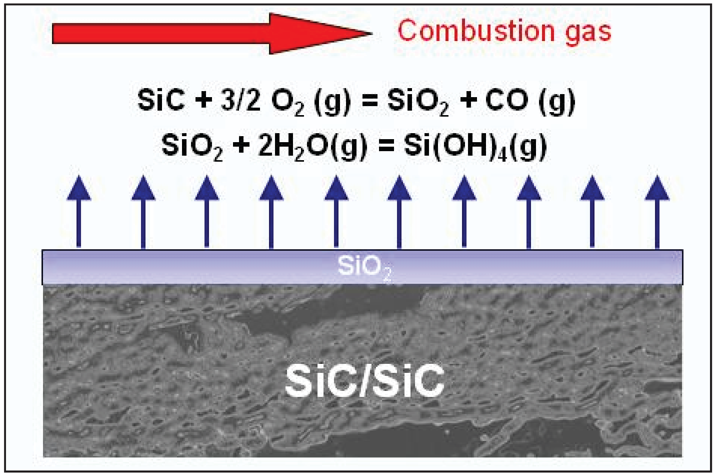


Work was supported by the NASA Fundamental Aeronautics Program under the Aeronautical Sciences Project

Motivation

- Turbine engine materials require long lifetimes at elevated temperatures
- Ceramic matrix composites (CMCs) offer substantial benefits
  - Limited by water vapor attack
- Environmental barrier coatings (EBCs) are necessary to protect the underlying ceramic
- Candidate materials are limited
  - Need to be thin, stable and durable
- Traditional processing methods may not be able to meet the requirements
  - Plasma Spray-Physical Vapor Deposition (PS-PVD)





Plasma Spray - Physical Vapor Deposition (PS-PVD)

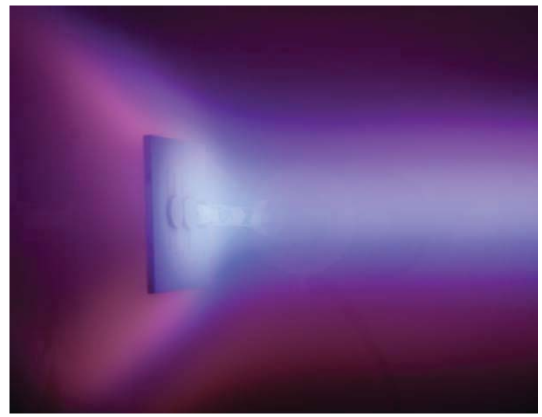
- Bridges the gap between plasma spray and vapor phase methods
  - Variable microstructure
  - Multilayer coatings with a single deposition

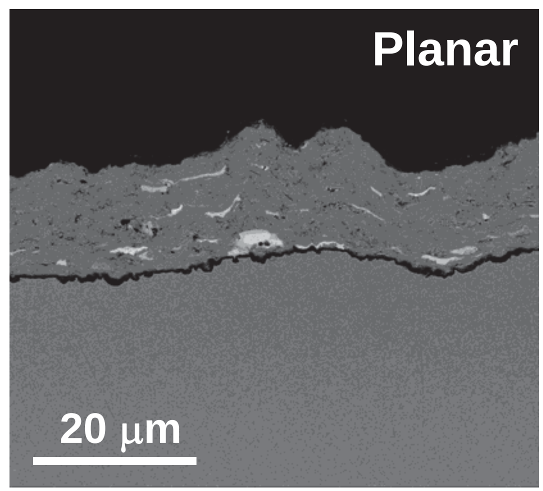
- Low pressure (70-1400 Pa)
  High power (>100 kW)
  - Temperatures 6,000-10,000K

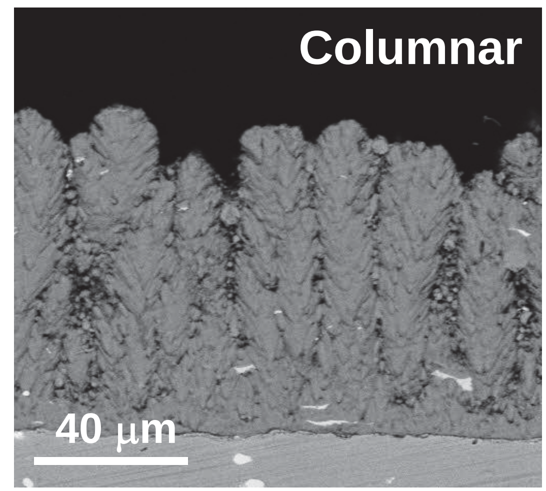
- High throughput[1]
  - 0.5 m^2 area, 10 μm layer in < 60s

- Material incorporated into gas stream
  - Non line-of-sight deposition

- Attractive for a range of applications
  - Solid oxide fuel cells, gas sensors, etc.



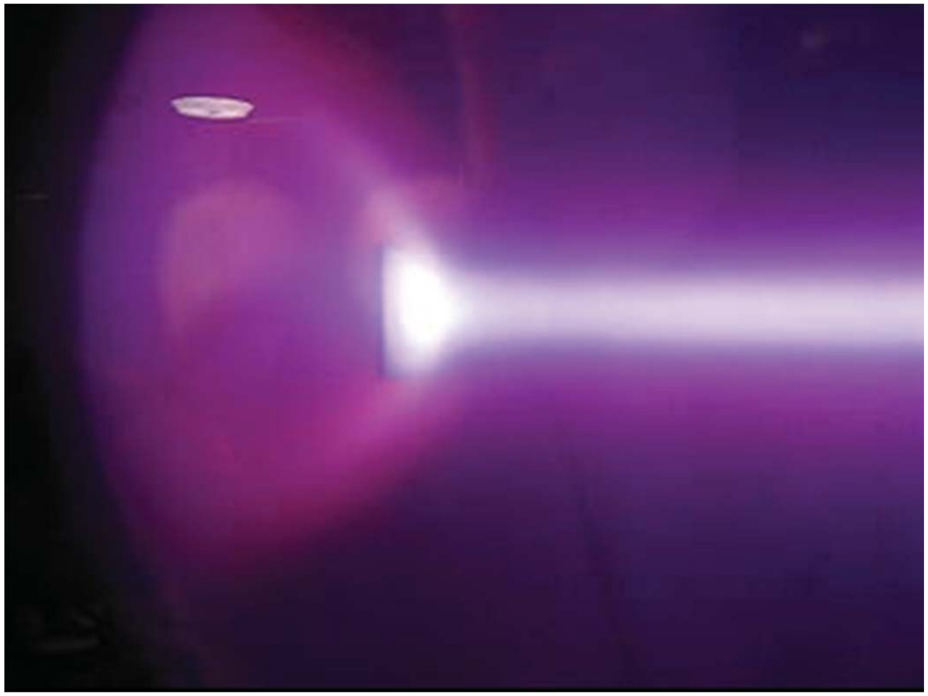




[1]A. Refke, et al. *Proceedings of the International Thermal Spray Conference, May 14-18,* (Beijing, China), 705-10 (2007).

Plasma Spray - Physical Vapor Deposition (PS-PVD)

- Bridges the gap between plasma spray and vapor phase methods
  - Variable microstructure
  - Multilayer coatings with a single deposition
- Low pressure (70-1400 Pa)
  High power (>100 kW)
  - Temperatures 6,000-10,000K
- High throughput[1]
  - 0.5 m^2 area, 10 μm layer in < 60s
- Material incorporated into gas stream
  - Non line-of-sight deposition
- Attractive for a range of applications
  - Solid oxide fuel cells, gas sensors, etc.

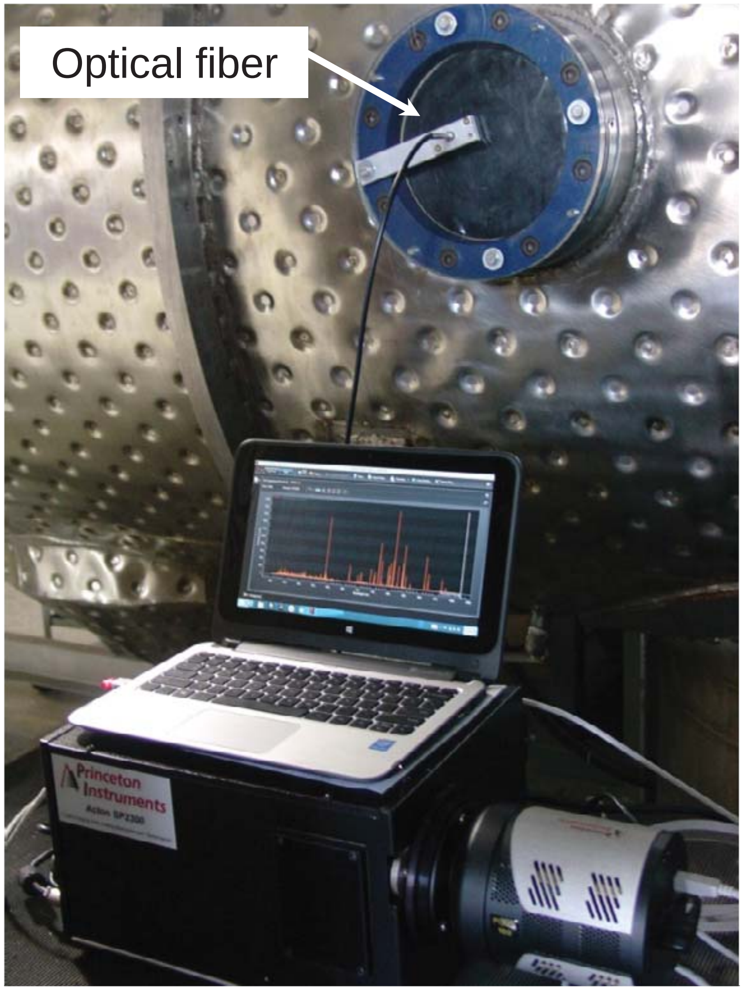


[1]A. Refke, et al. *Proceedings of the International Thermal Spray Conference, May 14-18,* (Beijing, China), 705-10 (2007).

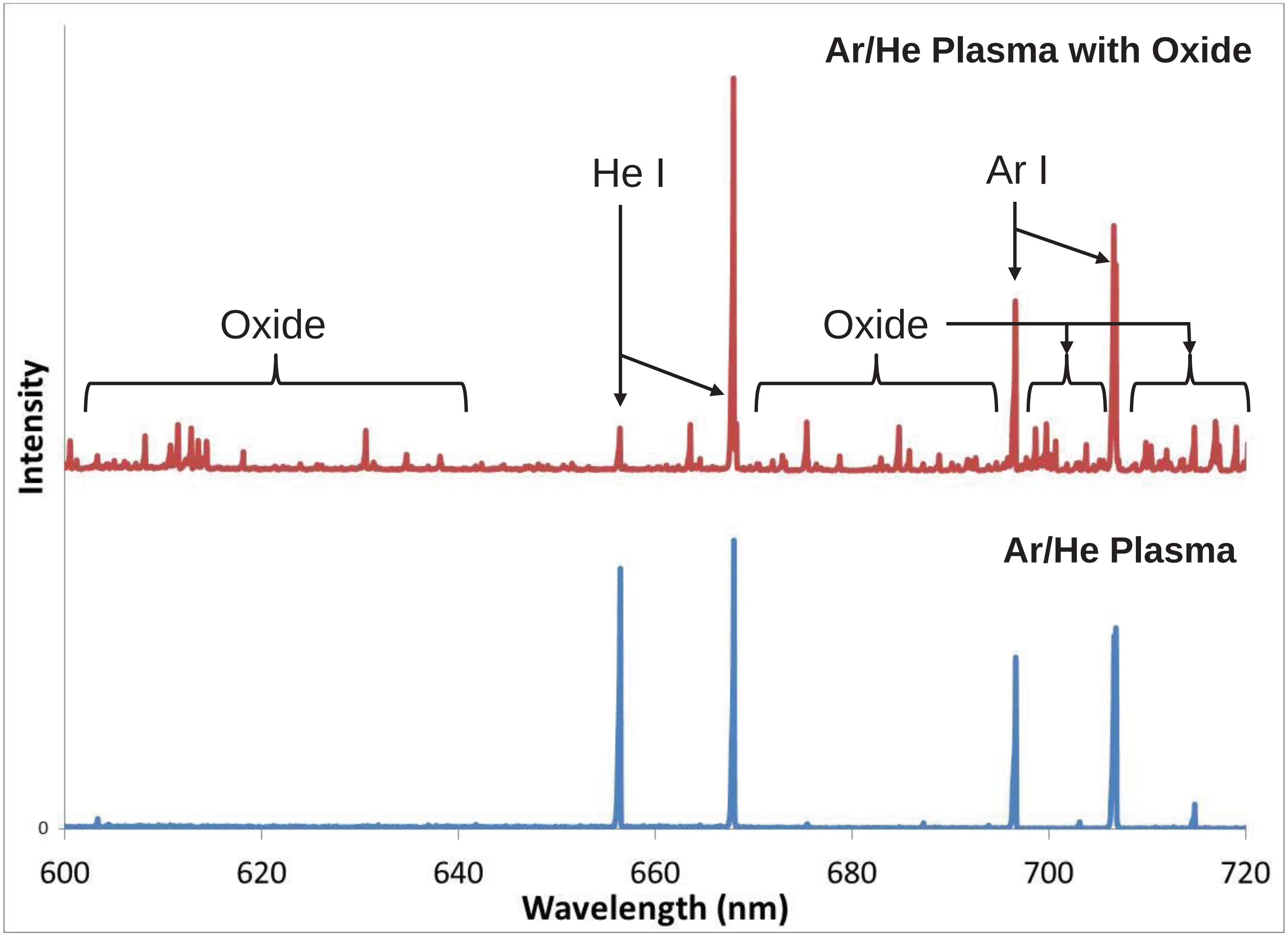
PS-PVD Diagnostics

Optical Spectrometer

- Data collected *in-situ*
- Emission lines measured and tracked
  - Plasma gases and feedstock
- Conditions can be optimized for maximum vaporization



PS-PVD Diagnostics



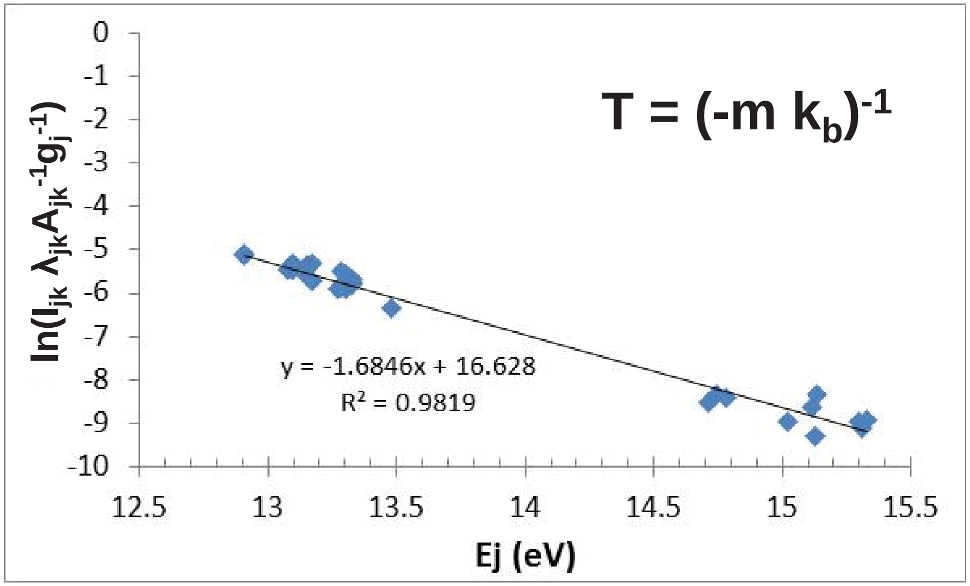
PS-PVD Diagnostics

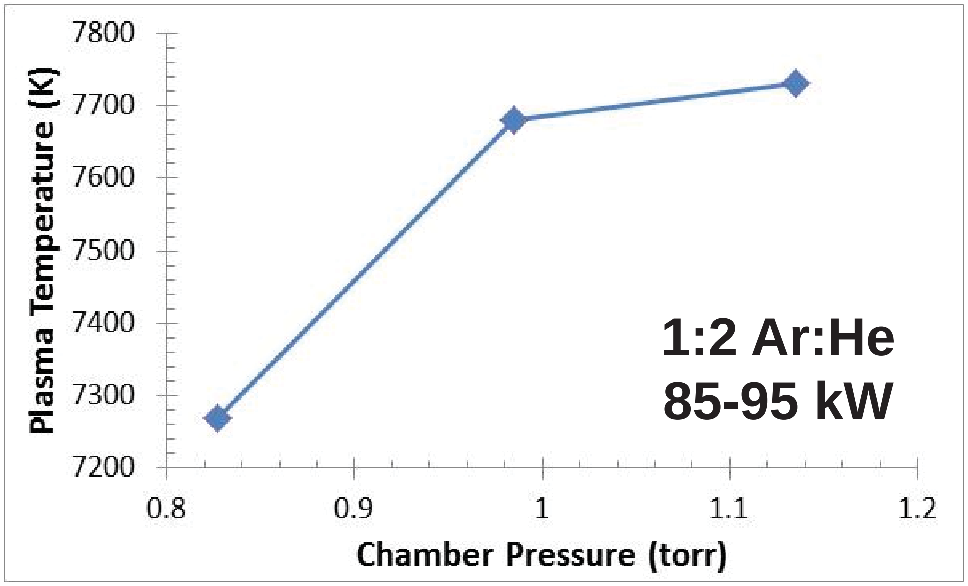
<u>Optical Spectrometer</u>

- Data collected *in-situ*
- Emission lines measured and tracked
  - Plasma gases and feedstock
- Conditions can be optimized for maximum vaporization

<u>Plasma temperature measurement</u>

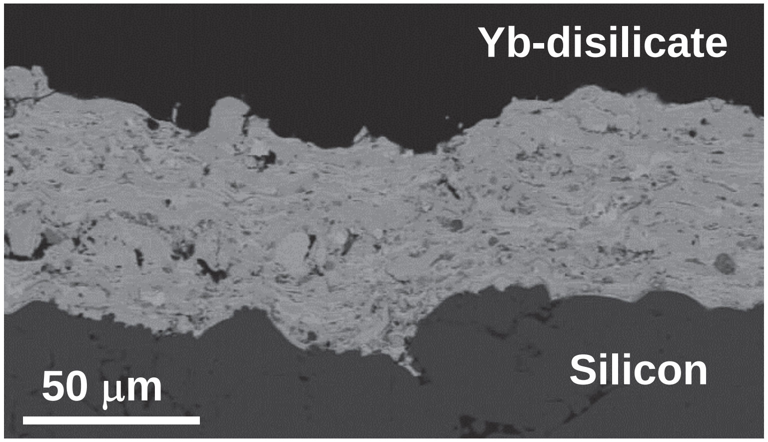
- Boltzmann distribution
- Assumes local thermal equilibrium
- Intensities of Ar I lines were used
  - 40 lines measured
  - 516 - 968 nm range

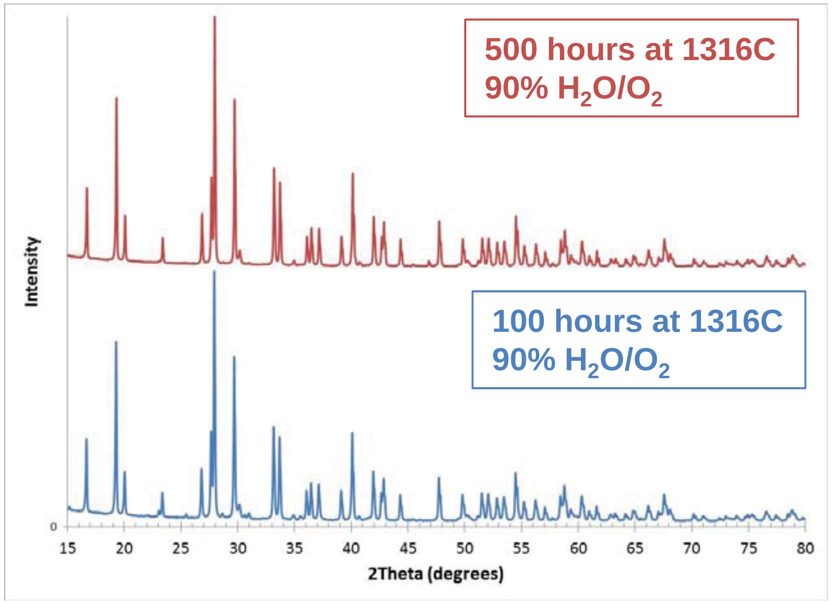




$Yb_2Si_2O_7$: As-Deposited

- $Yb_2Si_2O_7$ (Yb-disilicate) has been considered as a potential next-generation EBC
- Deposited using PS-PVD processing (~115 μm)
  - Air plasma sprayed silicon bond coat (~75 μm)
  - SiC/SiC substrate
- Splat-like deposition with large porosity distribution
- Backscatter shows some localized variation in Si content
  - Bright regions are Si-deficient
  - Dark regions are Si-rich
- XRD shows coatings are fully disilicate after heat treating
  - Isothermal exposure to water vapor at 1316C for 500 hours shows little crystallographic change



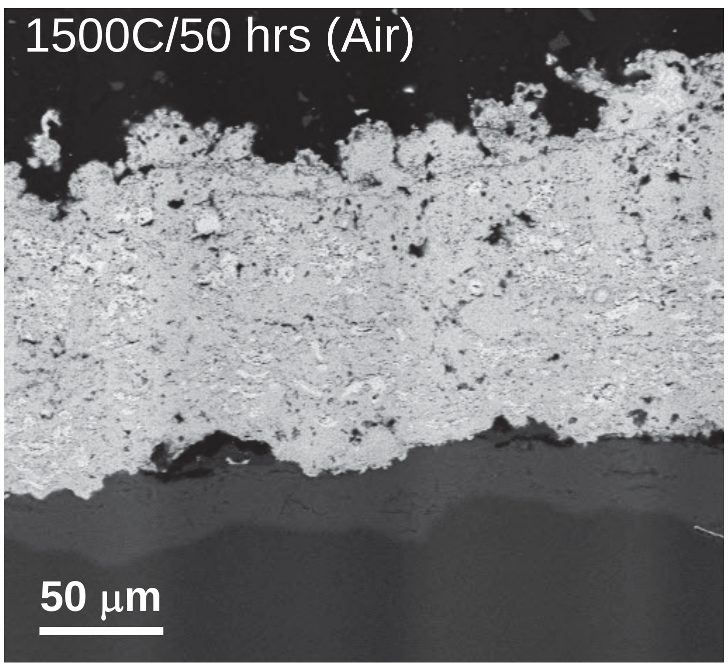


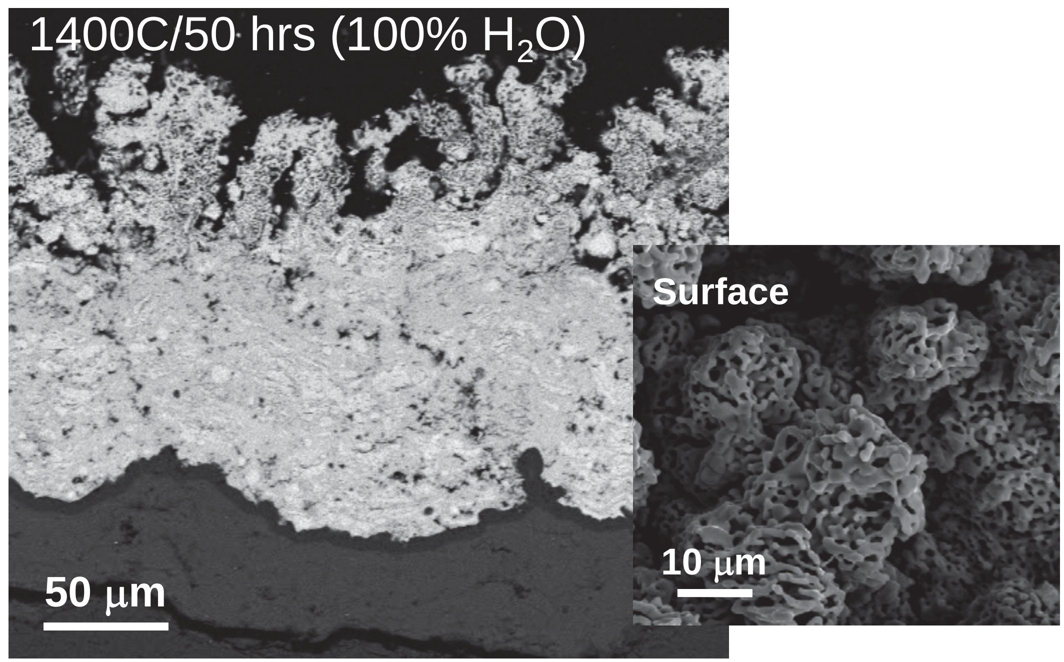
Single Layer Yb-disilicate EBCs

- High heat flux testing showed increased degradation of Yb-silicate coatings

- Coatings tested in air and in a steam environment from 1400-1500C
  - Yb-disilicate was stable in air with some sintering and delamination at the bond coat
  - Steam environment testing resulted in significant porosity at the surface due to the formation of Si-hydroxide

- Although Yb-disilicate has some desirable properties as an EBC, its silica activity may still be too high for temperatures required for advanced engine components.





Qualitative Ranking of Candidate EBC Materials

HfO_2
ZrO_2 [YSZ]
$2(Lu_2O_3) \cdot 3(ZrO_2)$
$2(Y_2O_3) \cdot 3(ZrO_2)$
$3(Yb_2O_3) \cdot 5(Al_2O_3)$
$3(Y_2O_3) \cdot 5(Al_2O_3)$ (yttrium-aluminum-garnet)
$Lu_2O_3 \cdot SiO_2$
$Yb_2O_3 \cdot SiO_2$
$Y_2O_3 \cdot SiO_2$
$Al_2O_3 \cdot TiO_2$
$2(Lu_2O_3) \cdot 3(HfO_2)$
$Lu_2O_3 \cdot 2(SiO_2)$
$Y_2O_3 \cdot 2(SiO_2)$
$Yb_2O_3 \cdot 2(SiO_2)$
$Ba(Sr)O \cdot Al_2O_3 \cdot 2(SiO_2)$ (barium-strontium-aluminosilicate)
$SrO \cdot Al_2O_3 \cdot 2(SiO_2)$ (strontium-aluminosilicate)
Al_2O_3
$3(Al_2O_3) \cdot 2(SiO_2)$ (mullite)
TiO_2
$CaO \cdot 2(Yb_2O_3) \cdot 3(SiO_2)$
$x(CeO_2) \cdot (ZrO_2)$
SiO_2
Cr_2O_3

Best Water Vapor Resistance

If silicon-free oxides can be adapted as EBCs, significantly higher stabilities are possible

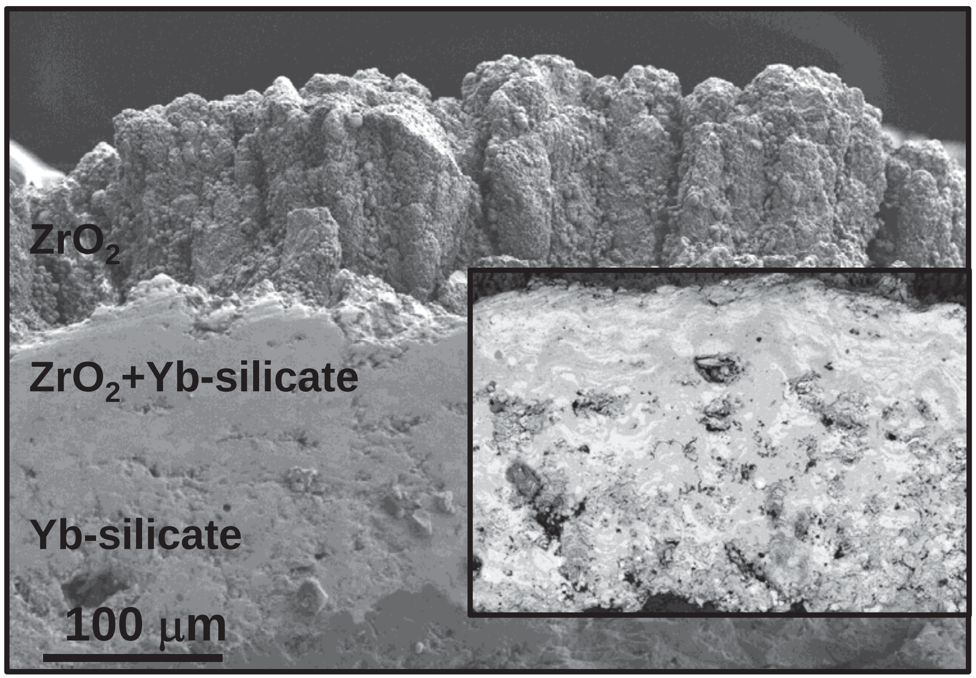
$$Flux = 0.664\left(\frac{v_\infty \rho_\infty L}{\eta}\right)^{0.5}\left(\frac{\eta}{D_{Si(OH)_4}\rho_\infty}\right)^{0.33}\frac{D_{Si(OH)_4}}{RTL}K\,a_{SiO_2}\left(P_{H_2O}\right)^2$$

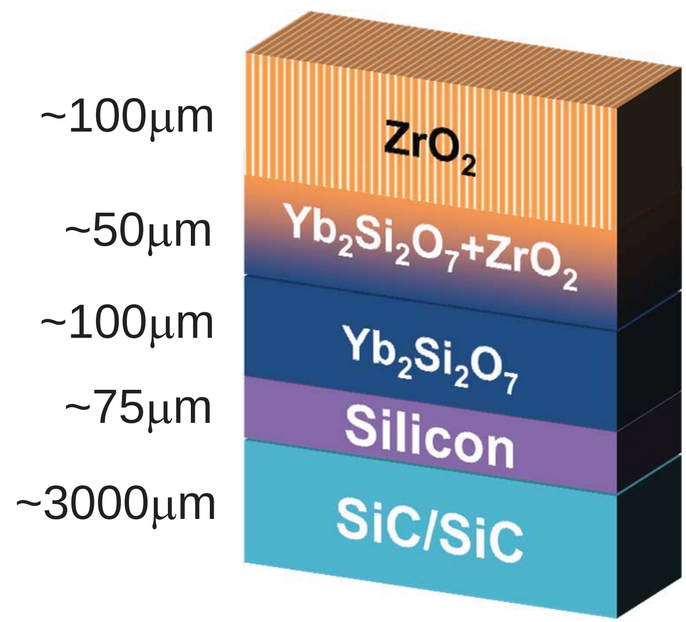
Under relevant turbine engine conditions:
Silicon Carbide: J = 0.48 mg/cm^2-hr
$Y_2SiO_5 + Y_2Si_2O_7$: J = 0.12 mg/cm^2-hr
$Y_2Si_2O_5 + Y_2O_3$ J = 2 x 10^{-4} mg/cm^2-hr (CTE issues)

Compiled by Jim Smialek in Review: N. Jacobson et al. ASM Handbook 13B, 565 (2005)

T/EBC Multilayer Coatings

- Rare earth silicates have some desirable properties for EBCs, but SiO_2 activity may still be too high for temperatures required for advanced engine components.
- The addition of an oxide layer on the surface shows promise for reducing the temperature of the EBC and improving durability.
- Topcoat of rare earth doped t' ZrO_2 provides erosion resistance equaling or surpassing other vapor processed coatings
- Columnar microstructure in the topcoat reduces the in-plane modulus to a value of 25-30GPa





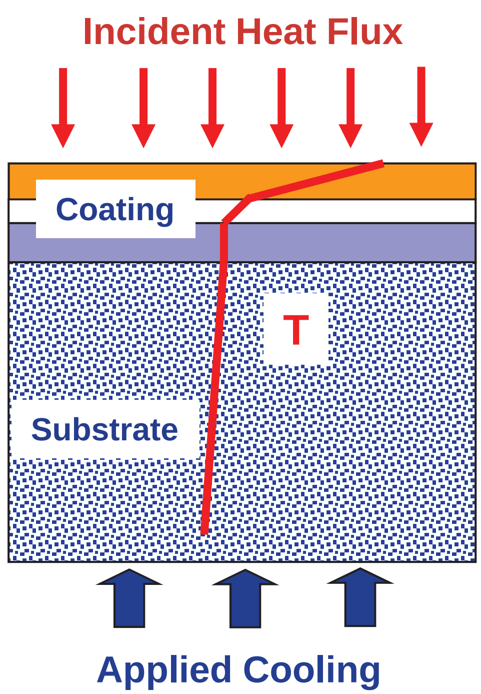
Thermal Conductivity Testing

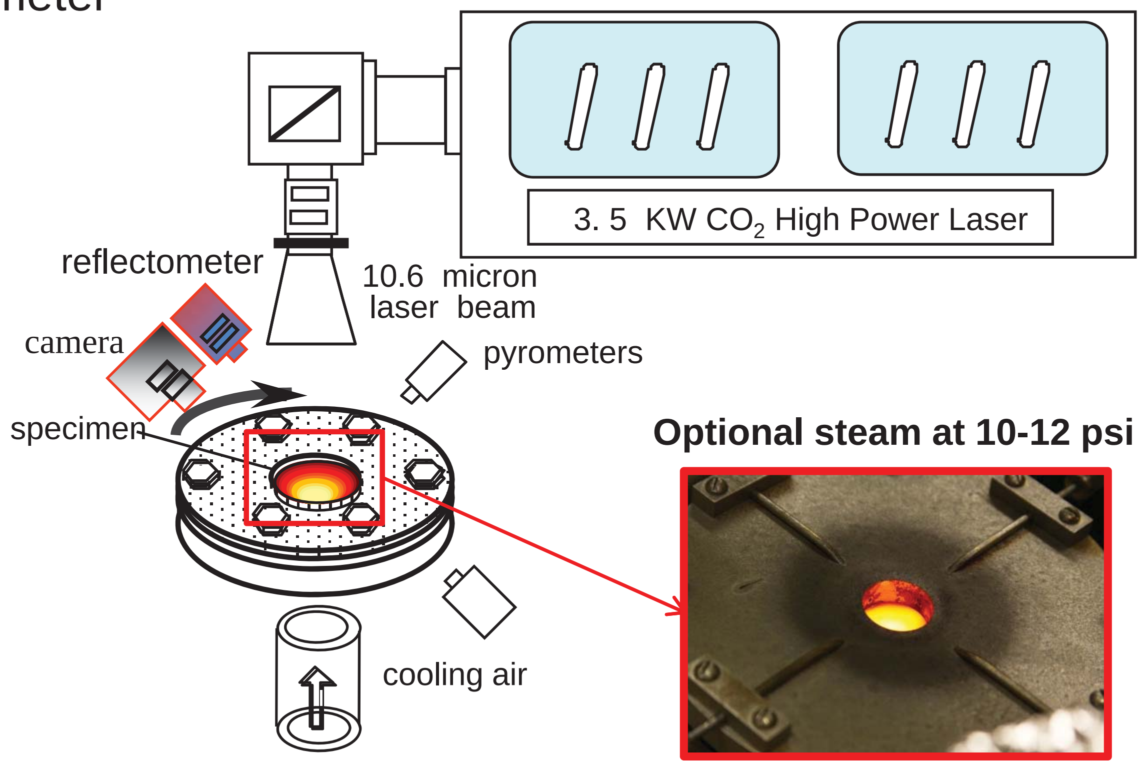
- In situ measurement
- 8 μm pyrometer on the surface and backside
- High power CO_2 laser high-heat-flux system
  - Capable up to 315 W/cm^2
- Sample approximately 1” in diameter

$$k_{ceramic}(t) = q_{thru} \cdot l_{ceramic} / \Delta T_{ceramic}(t)$$

$$q_{thru} = q_{delivered} - q_{reflected} - q_{radiated}$$

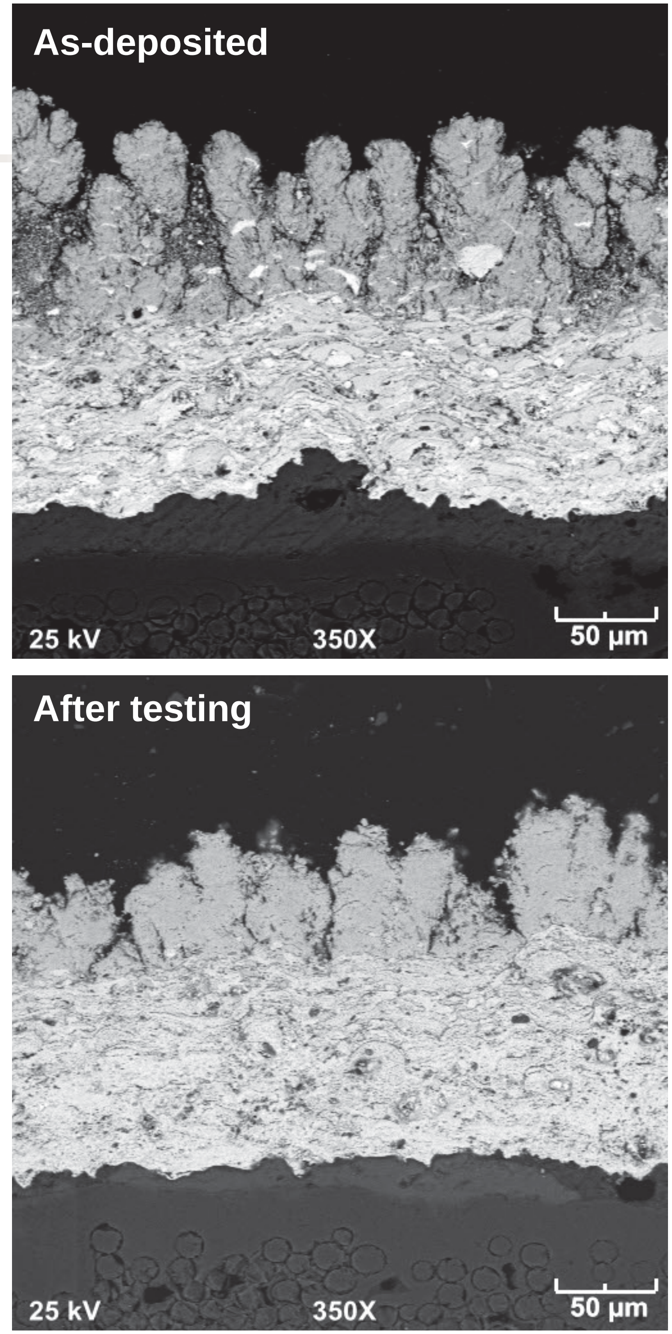
$$\Delta T_{ceramic}(t) = T_{ceramic-surafce} - T_{metal-back} - \int_0^{l_{bond}} \frac{q_{thru} \cdot dl}{k_{bond}(T)} - \int_0^{l_{substrate}} \frac{q_{thru} \cdot dl}{k_{substrate}(T)}$$





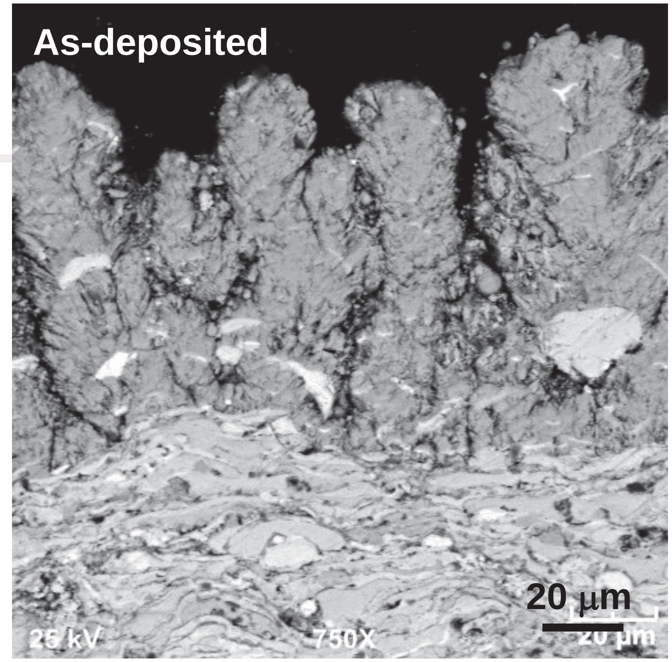
3-Layer T/EBC

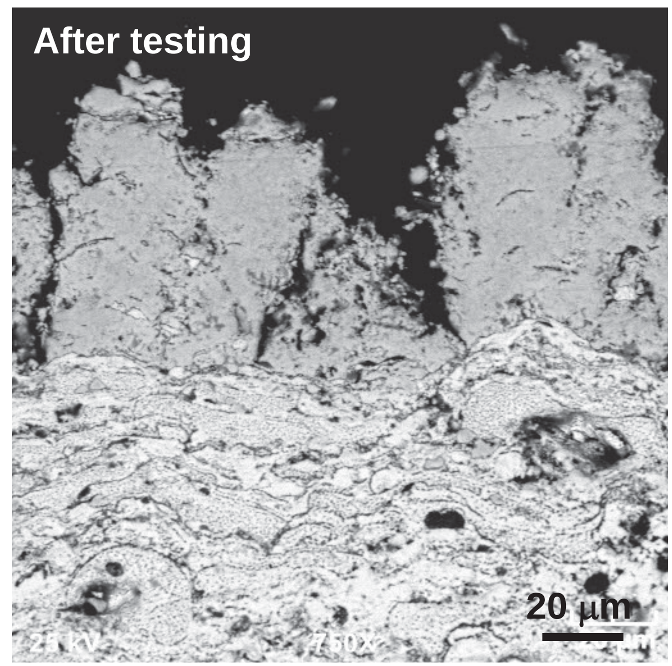
- Sample surface heated with high heat flux laser
  - Provides thermal gradient
- Tested for 10 heating cycles (1 hour each)
  - 1470C surface temperature
  - 1350C interface temperature
  - 1150C backside temperature
- Microstructure showed some changes due to the gradient testing
  - Doped ZrO_2 topcoat sintered
  - $Yb_2Si_2O_7$ EBC layer did not change
  - Silicon bond coat showed signs of melting in various locations
- Sintering also observed in thermal conductivity measurement
  - k_0: 1.75 W/mK
  - k_{10}: 2.15 W/mK

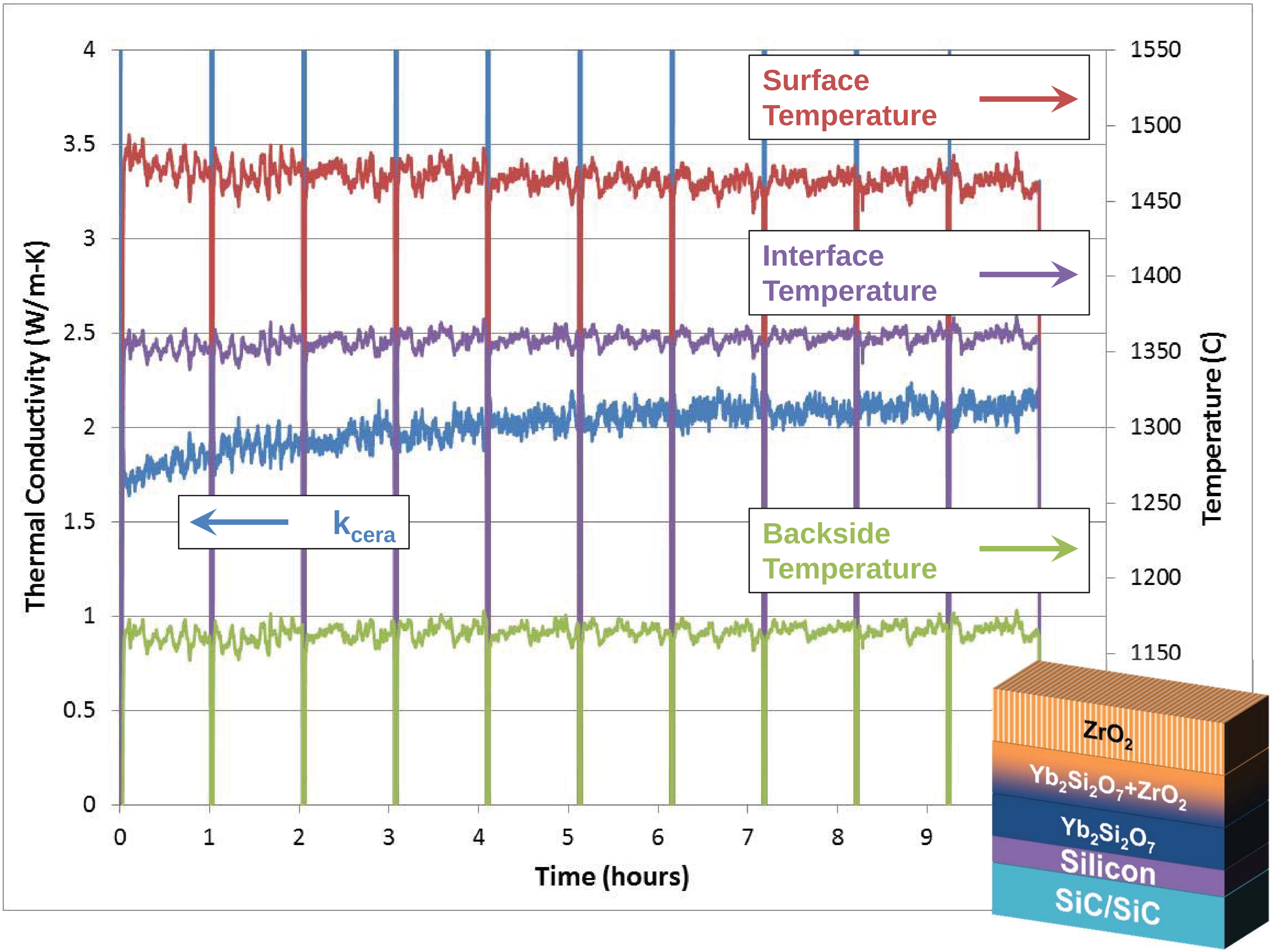


3-Layer T/EBC

- Sample surface heated with high heat flux laser
  - Provides thermal gradient
- Tested for 10 heating cycles (1 hour each)
  - 1470C surface temperature
  - 1350C interface temperature
  - 1150C backside temperature
- Microstructure showed some changes due to the gradient testing
  - Doped ZrO_2 topcoat sintered
  - $Yb_2Si_2O_7$ EBC layer did not change
  - Silicon bond coat showed signs of melting in various locations
- Sintering also observed in thermal conductivity measurement
  - k_0: 1.75 W/mK
  - k_{10}: 2.15 W/mK

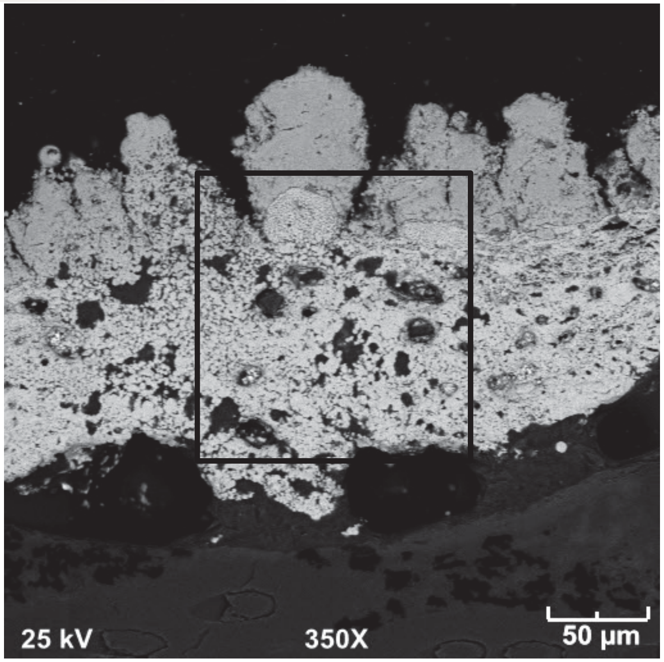


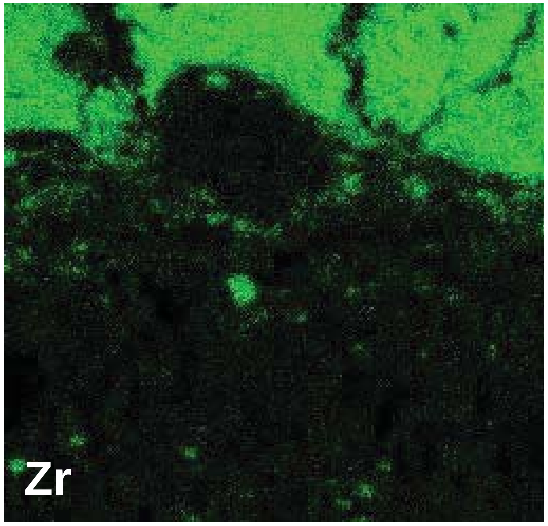


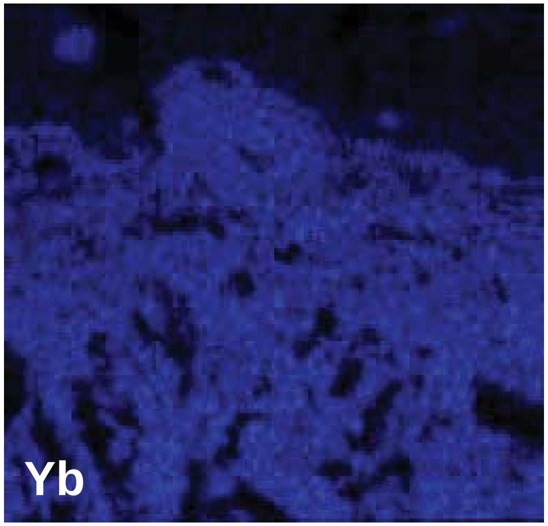

Surface Temperature
Interface Temperature
Backside Temperature
k_{cera}
Thermal Conductivity (W/m-K)
Temperature (C)
Time (hours)
4
3.5
3
2.5
2
1.5
1
0.5
0
1550
1500
1450
1400
1350
1300
1250
1200
1150
0 1 2 3 4 5 6 7 8 9
ZrO_2
$Yb_2Si_2O_7+ZrO_2$
$Yb_2Si_2O_7$
Silicon
SiC/SiC

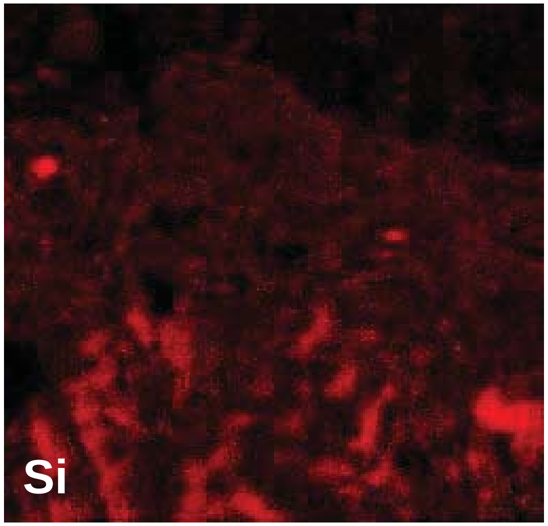
Silicon Infiltration

- Microstructure indicated melting of Si bond coat
  - Silicon infiltration of Yb-silicate layer
  - Rapid sintering and delamination
- 1370C maximum calculated interface temperature
  - Impurities would suppress the melting temperature from 1410C
- Delamination isolates the top layer oxide and increases sintering









Conclusions and Future Work

- PS-PVD processing is a promising technique for depositing next-generation thermal and environmental barrier coatings on advanced engine components.
- The addition of a more thermally capable oxide topcoat on RE-silicate materials could improve performance as a T/EBC.
- The low melting silicon bond coat is the limiting factor for these coatings with surface temperatures approaching 1500C.
- Future T/EBCs will use a more thermally capable bond coat, which should allow for thinner coatings and better performance, and will be tested under steam conditions and under mechanical loading with thermal gradient.